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(54) PHOTOSENSITIVE COMBINATION OF ELEMENTS SUITED FOR USE IN RADIOGRAPHY

(71) We, AGFA-GEVAERT, a naamloze vennootschap organised under the laws of Belgium, of Septestraat 27, B2510 Mortsel, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an improved combination of photosensitive elements suited for use in radiography and more particularly to a combination comprising an X-ray intensifying screen of the fluorescent type and a silver halide recording element.

From the published German Patent Application 2,051,262 filed October 19, 1970 by Kodak Ltd. a radiographic combination of intensifying screen and silver halide-containing element is known, which employs a relatively low silver halide content and phosphors capable of emitting more than half of their radiant energy in the near ultraviolet region at wavelengths less than about 410 nm.

According to said application an improved method for rapid processing of photographic films and improved roller transport of the processed silver halide containing elements is provided. Because of the relatively low silver halide content shorter developing and fixing times are possible and the risk of mechanical damage of the gelatin silver halide emulsion layer that may occur in a roller transport processor is reduced.

According to said German Patent Application the silver halide recording material is capable of producing a negative silver image in situ having a covering power, (as hereafter defined) greater than about 50, the silver halide being present in an equivalent concentration of less than about 0.080 g of silver per sq.dm.

However the use of photographic materials with a low silver halide content and high covering power has the result that the speed is rather low since the desired high covering power is obtained with fine-grained silver halide emulsions that inherently have a lower photographic speed than coarse-grained emulsions (ref. P. Glafkidès, Photographic Chemistry, Vol. 1 (1958) 89—90).

In low dose X-ray photography applied for medical X-ray purposes the advantages associated with the use of low content silver halide emulsions can only be obtained by the use of intensifying screens that have a particularly high intensification factor.

It has been established, however, that the use of intensifying screens that have more than half their spectral emission below 410 nm such as the lead-activated barium sulphate screens described, e.g., in the United States Patent 2,887,379 of Ralph Kingsley Blake and Francis Peter Alles issued May 19, 1959 and introduced by Du Pont in 1948 in the faster CRONEX (trade name) Hi-Speed screens and the lead-activated strontium sulphate screens and europium-activated barium strontium sulphate screens described in said published German Patent Application 2,051,262 although strongly emitting in the inherent sensitivity range of the silver halide have not emission power that is sufficient for allowing their combined use with low content silver halide materials in low dose X-ray photography.

Other screens containing terbium-activated gadolinium oxysulfide phosphors emitting more than 50% of their energy above 410 nm wavelength, more particularly in the green light spectral region, as described in the published German Patent Application (Dt—OS) 2,326,617 filed May 25, 1973 by Agfa-Gevaert AG, although having a particularly high intensification factor are less suitable since they need specially spectrally sensitized silver halide emulsions that have to be processed in nonpractical dark-room conditions i.e. in red light.

It is an object of the present invention to provide a novel and improved radiographic combination of a fluorescent screen and a photosensitive element of low silver halide content, which combination is suitable for low dose X-ray photography and needs no special darkroom conditions in the processing of the silver halide material.

Another object of this invention is to provide a radiographic process wherein the time required to obtain a developed image is reduced and the effective life time of the processing solutions is prolonged.

Another object of this invention is to provide a radiographic screen-silver halide film combination offering higher speed for a given image sharpness quality as compared with a combination of a prior art screen and an identical silver halide film in which the silver halide is not spectrally sensitized with sensitizing dyes.

In accordance with the present invention these objects are attained with a combination of photosensitive materials suitable for radiography and comprising:

a silver halide photographic material comprising a support and silver halide which is capable of producing in said material a negative silver image having a covering power (as hereafter defined) greater than about 50 and is present in an equivalent concentration of less than about 0.080 g of silver per sq.dm, e.g. between 0.080 and 0.030 g of silver per sq.dm, and at least one radiographic intensifying screen material, which contains a phosphor layer comprising a phosphor or a phosphor-mixture consisting wholly or mainly of a rare earth metal-activated lanthanum oxychloride or lanthanum oxybromide, e.g. a terbium- or terbium and ytterbium-activated lanthanum oxychloride or lanthanum oxybromide, said lanthanum oxyhalide phosphors optionally also being activated with cerium and said phosphor or phosphor mixture having more than half its spectral energy emission above about 410 nm wavelength, more than half its visible light spectral emission energy between 400 and 500 nm and its maximum energy emission peak below 500 nm, and wherein said phosphor layer has a coverage of said lanthanum oxyhalide phosphor of 100 to 800 g per sq.m and said screen material has an intensification factor of at least 20 at 40 kV and at least 25 at 80 kV.

In relation to the present invention as above defined attention is directed to United Kingdom Patent No. 1,319,569 in claim 1 of which there is claimed: "A rare earth oxyhalide phosphor having the general formula:

$$M_{1-w-y}OX : Tb_wYb_y$$

wherein:
M is La and/or Gd;
X is Cl and/or Br;
w is from 0.0005 to 0.03 moles per mole of the phosphor host matrix; and
y is from 0.00005 to 0.005 moles per mole of the phosphor host matrix".

Combinations of materials according to the invention as hereinbefore defined can be used not only in radiography by means of X-rays, but also in radiography by means of other non-visible penetrating radiation e.g. β-rays, γ-rays or fast electrons, e.g. as obtained in an electron microscope.

By "intensification factor" is to be understood a value obtained by dividing the radiation dose required for producing without the aid of an intensifying screen a silver image of given density (Density: 1.00), by the radiation dose required to produce a silver image of the same density with the aid of the intensifying screen, the wavelength distribution of the radiation and the development conditions being the same in the two cases.

By the term "covering power" is understood the reciprocal of the number of grams of silver per sq.dm divided by the maximum optical density of the silver image obtained.

Barium lead sulphate screens, e.g. Kodak Type 80 Intensifying Screens (see the advertising brochure of Kodak "X-Ray Intensifying Screens" for Medical Radiography (1958) p.6, and europium-activated barium strontium sulphate phosphor screens as described, e.g. in the published German Patent Application 2,051,262 as mentioned above, absorb a large fraction of the incident X-ray energy and emit violet light and ultraviolet radiation to which the X-ray silver halide film is highly sensitive. Therefore, in high speed screen/film systems they have been preferred up till now over the calcium wolframate screens emitting mainly blue light.

In practice, the intensifying fluorescent screens used for medical X-ray purpose together with the radiographic silver halide materials are almost exclusively screens that comprise calcium wolframate, lead barium sulphate or europium-activated barium strontium sulphate as phosphor, because the skilled worker in the art has never questioned the superiority of these screens over the large variety of screens comprising other types of phosphors emitting ultraviolet radiation or blue light.

It has been established experimentally that some of such other phosphors are in fact preferable to those customarily used. For example the blue light-emitting terbium-activated lanthanum oxyhalide phosphors in which the terbium oxyhalide content is not more than 0.006 mole per mole of the total oxyhalide, yield with non-spectrally sensitized silver halide films an improved speed for same image sharpness value as compared with the phosphors mainly emitting ultraviolet radiation known from the published German Patent Application 2,051,262 as mentioned above viz. the europium-activated barium strontium sulphate screens.

Particularly useful phosphors for use according to the present invention is an X-ray fluorescent intensifying screen are therefore represented by the following general formula:

$$La_{(1-n)} \cdot Tb_n^{+3}\, OX$$

wherein:

X is chlorine or bromine

Tb^{+3} is trivalent terbium, and

n is 0.0001 to 0.006.

The halogen X is preferably present in the range from 97.5 to 100% of the stoichiometric amount.

Phosphors that particularly strongly emit blue light are lanthanum oxybromide phosphors that have been activated with small amounts of terbium, e.g. with 0.002 gram atoms of terbium per gram atom of lanthanum and in which the ratio of gram atoms of oxygen to gram atoms of bromine is 1:1.

Cerium may replace lanthanum in an amount as described in the United Kingdom Patent 1,247,602 filed October 9, 1969 by General Electric Company, e.g. it may be present in an amount from 0.1 to 0.8 mole percent based in the phosphor composition.

The preparation of terbium-activated lanthanum oxychloride and lanthanum oxybromide phosphors is described in said United Kingdom Patent 1,247,602, French Patents 2,021,398 filed October 23, 1969 by General Electric Company and 2,021,399 filed October 23, 1969 by General Electric Company, and published German Patent Applications 1,952,812 filed October 21, 1969 by General Electric Company and 2,161,958 filed December 14, 1971 by General Electric Company.

Information concerning various fluorescent screens is given in graphical form in the accompanying drawings, in which:

Fig. 1 represents an emission spectrum relating to an activated lanthanum oxybromide which is useful for carrying out the present invention;

Fig. 2 comprises graphs in which the photographic speed of different phosphors I, II and III (referred to in the Example given later herein) is plotted against the phosphor content of such screens; and

Fig. 3 comprises graphs in which the square wave response factor (SWRF) of the said phosphors I, II and III is plotted against their photographic speed (S).

The phosphor whose emission spectrum is shown in Fig. 1 is a lanthanum oxybromide containing stoichiometric amounts of oxygen and bromine and activated with 0.002 gram atoms of terbium per gram atom of lanthanum. In the graph, the relative emission energies (I) at various wavelengths (nm), responsive to ultraviolet radiation of 313 nm wavelength, have been plotted on a percentage basis, taking the value of the energy emission at the maximum energy emission peak as 100%.

Other particularly useful phosphors for application according to the present invention are described in the published German Patent Application 2,161,958 filed December 14, 1971 by General Electric Company corresponding with the Canadian Patent 927,089 filed April 11, 1972 by General Electric Company. These phosphors are terbium and ytterbium-activated lanthanum oxychlorides or lanthanum oxybromides corresponding to the following general formula:

$$La_{1-w-y}OX{:}Tb_wYb_y$$

wherein:

X is chlorine or bromine

w is from 0.005 to 0.006 mole per mole of the oxyhalide, and

y is from 0.00005 to 0.005 mole per mole of the oxyhalide.

The presence of the ytterbium strongly reduces the afterglow effect that follows the X-ray irradiation so that the formation of ghost images in excluded and sharper images are obtained. The preparation of this class of phosphors has been described in the published German Patent Application 2,161,958 as mentioned above. Particularly interesting for the purpose of the present invention are said phosphors wherein w is 0.002.

The screen-film combination of the present invention among other things has the following advantages in comparison with commercial screen-film systems:

(1) low silver halide content resulting in less expensive silver halide materials that have the already mentioned advantages with regard to rapid processing and roller transport;

(2) reduced X-ray dose;
As a consequence of lower X-ray dose for obtaining a same image density shorter exposure times can be applied, which is interesting for producing non-blurred images of moving objects. In addition, the lower X-ray dose is particularly important in medical X-ray applications in which harmful biological action of the radiation is to be excluded or to be kept at a minimum.

(3) by the possibility of decreasing the exposure time an additional gain in image sharpness can be obtained, which is due to the decrease of the well-known Schwarzschild-effect in the silver halide material;

(4) the possibility of reducing the voltage of the X-ray tube, which gives rise to an increase of contrast without need for a higher X-ray dose;

(5) the possibility of increasing the voltage of the X-ray tube whereby the X-ray dose can be lowered without impairing the contrast;

(6) the possibility of obtaining improved sharpness at usual X-ray dose by eliminating scattered radiation with a more selectively operating scatter grid. Since the scatter grid (Potter-Bucky diaphragm) attenuates the radiation intensity it is important to employ a phosphor with high conversion of X-ray radiation energy into visible light;

(7) the possibility of increasing at usual X-ray dose the object to film distance involving image magnification. This is efficient mainly when an X-ray tube with small focus is used. However, such tubes having only a low X-ray emission capacity bring about the need of a long exposure time when known screen-film combinations are used and so could only be used up till now for radiography of non-moving objects (extremities);

(8) the possibility when operating with a usual X-ray dose of using in the silver halide materials filtering dyes that increase the image sharpness;

(9) the possibility of using single-side coated silver halide emulsion films, which do not suffer from the "cross-over" effect that is characteristic for double-side coated silver halide materials and will be explained below.

The fluorescent screen materials for use according to the present invention include such materials wherein the lanthanum oxyhalide phosphor is mixed with yttrium oxysulphide phosphor activated with terbium. The preparation of phosphors of the latter type has been described in the French Patent 1,580,544 field July 25, 1968 by N.V. Philips' Gloeilampenfabrieken, in the United States Patents 3,418,246 of Martin R. Royce issued December 24, 1968 and 3,418,247 of Perry N. Yocom issued December 24, 1968 and in the United Kingdom Patent 1,247,602 as already mentioned before.

In a combination of intensifying screen(s) and silver halide material according to the present invention the fluorescent screen(s) and the silver halide material may be separate elements or they may be integral parts of one element.

The radiographic material may comprise a radiation-sensitive silver halide emulsion either on only one side or on both sides of the support. Intensifying screens may be provided on both sides of a single- or double-coated radiographic material. The radiographic combination of fluorescent screens and photosensitive material may further comprise the frequently used intermediate and/or protective and/or stripping layers, which may be arranged between or over the radiation-sensitive emulsion layer(s) and the fluorescent screen(s).

Particles of the selected phosphor or phosphor mixture may be disposed in a binder which forms a layer on a support or forms a self-supporting layer (i.e. a sheet). Suitable layers or sheets have a thickness of preferably 0.05 to 0.5 mm and contain the fluorescent substance(s) or phosphors dispersed in a binder in an amount preferably of 80 to 95% by weight. Such binder is, e.g., an organic high molecular weight polymer. Suitable binding agents are, e.g., cellulose nitrate, ethylcellulose, cellulose acetate, polyvinyl acetate, polystyrene, polyvinyl butyral, polymethyl methacrylate and the like.

A preferred grain size of the fluorescent substances is preferably in the range of about 1—25 microns.

The surface of the fluorescent material layer may be protected against moisture and mechanical damage by a coating of an organic high polymer applied to a thickness of 0.001 to 0.05 mm. Such protecting coating is, e.g., a thin film of cellulose nitrate, cellulose acetate, polymethyl methacrylate and the like.

A disadvantage of silver halide photographic materials having low silver halide content lies in the increase of "cross-over", a phenomenon associated with silver halide emulsion materials carrying at both sides of a support that is transparent for fluorescent light a silver halide emulsion layer, which during the X-ray exposure stands in close contact with a fluorescent screen.

Indeed, the light emitted by one of these fluorescent screens gives rise not only to an image-wire blackening in the adjacent silver halide emulsion layer, but also penetrates to a considerable extent through the relatively thick support and produces an unsharp image in the oppositely situated silver halide emulsion layer. This phenomenon is called "cross-over". The degree of cross-over substantially determines the quality of the image obtained in the radiographic material.

The cross-over image is unsharp because of the diffusion of light in the support sheet and in the different layers of the recording material and also because of the diffuse refraction and reflection of light taking place at the boundaries of said layers and support sheet.

In order to diminish the cross-over, at least one layer and/or the base material of the light-sensitive material of the present invention will preferably contain a dye called hereinafter "filtering dye" absorbing light in the wavelength range emitted by the fluorescent screen and used in the combination.

The filtering dyes used in the silver halide emulsion recording material are preferably incorporated in the hydrophilic colloid layer between the silver halide emulsion layers or in the emulsion layers themselves. They may, however, also be incorporated in one or more subbing layers and even in the support. The dyes have, however, preferably such chemical and/or physical characteristics that they can be removed or decolorized in one of the processing baths.

According to a preferred embodiment of the present invention filtering dyes absorbing in the wavelength range of about 400 to 500 nm are used when fluorescent screens are applied that substantially emit light in the wavelength range of 400—500 nm.

The amount of filtering dye is preferably in the range of amounts that reduce the cross-over light in the above wavelength range to such a degree that its intensity becomes smaller than 30% of the intensity of the light impinging on an adjacent emulsion layer. For example 25 to 1000 mg of filtering dye(s) are used per sq.m but here likewise lower or higher amounts may be appropriate according to the result aimed at.

Suitable filtering dyes that can be removed from hydrophilic colloid layers are Tartrazine (C.I. Acid Yellow 23) and the dyes described in the United States Patent 3,624,229 of Daniel Maurice Timmerman, August Jean Van Paesschen and Albert Emiel Van Hoof issued November 30, 1971.

Cross-over is excluded when the silver halide is present in a single coating. Normally, however, a duplitized or dual coating is used, i.e. a photographic material having a silver halide emulsion layer on each side of a transparent support.

The spectral sensitivity of the silver halide emulsions may be enlarged or improved by spectral sensitizing in the wavelength range of 400 to 500 nm with common spectrally sensitizing dyes used in silver halide emulsions, which include cyanine dyes and merocyanine dyes as well as other dyes as described by F. M. Hamer in "The cyanine dyes and related compounds", Interscience Publishers (1964). These dyes are preferably used in an amount in the range of 20 mg to 250 mg per mole of silver halide.

The silver halide in the emulsion layer(s) may comprise varying amounts of silver chloride, silver iodide, silver bromide, silver chlorobromide, silver bromoiodide, and the like, but when coated must be capable, after exposure and processing, of producing a negative silver image remaining thereon, i.e. in situ. Particularly good results are obtained with silver bromoiodide emulsions in which the average grain size of the silver bromoiodide crystals is in the range of about 0.1 to about 3 μm.

When a duplitized silver halide coating is employed, preferably each such coating contains silver halide in an amount equivalent to an amount less than about 0.040 g of silver per sq. dm. When these layers are applied by means well-known in the art it is desirable in the combinations of our invention that the silver halide-containing coating or coatings be capable of transmitting less than about 40% and preferably less than about 30% of the incident radiation from the screen at wavelengths longer than 410 nm.

The proper transmittance can be obtained in a variety of ways, such as e.g. by the incorporation of optically separating barriers, e.g. undercoats, which can be positioned between the silver halide-containing layers, by altering the composition of said layers, by including dyes or other materials, by adjusting the halide balance or by modifying the silver halide grain shape, grain size, size distribution and the like.

The image-forming silver halide emulsion may be sensitized by any of the known procedures.

For the purpose of accelerating the development, the exposed photographic material may be developed in the presence of development accelerators. These development accelerators can be used either in the silver halide emulsion, in adjacent layer(s) or in the developing bath.

The exposed silver halide can with advantage be developed in an energetic surface developer. The high energy allows the development to proceed quickly and may be obtained by properly alkalizing the developing liquid (pH 9—12), by using high-energy developer. The high energy allows the developing substances having a synergistic effect.

The radiation-sensitive emulsions for use in the present invention may be coated on a wide variety of supports e.g. films of cellulose nitrate, cellulose esters, polyvinylacetal, polystyrene, polyethylene terephthalate and other polyester materials as well as α-olefin-coated papers, e.g. paper coated with polyethylene or polypropylene.

Preferred supports comprise a linear condensation polymer, blue coloured polyethylene terephthalate being an example thereof.

The support may be coated with subbing layers for improving the adhesion of the silver halide emulsion layer(s) thereto.

The following example illustrates the present invention.

Example.

A silver bromoiodide X-ray emulsion (1.5 mole % of silver iodide) was prepared in such a way that it contained silver halide grains with an average grain size of 0.65 μm and comprised per kg 74 g of gelatin and an amount of silver halide corresponding to 190 g of silver nitrate. As stabilizing agents the emulsion contained per kg 545 mg of 5-methyl-7-hydroxy-s-triazolo[1,5-a]-pyrimidine, 6.5 mg of 1-phenyl-5-mercaptotetrazole, and 0.45 mg of mercury cyanide. The covering power obtainable with said emulsion in the developing conditions defined hereinafter was 60.

This emulsion was coated on both sides of a double side subbed polyethylene terephthalate support in such a way that on each side of the support a silver halide emulsion layer was obtained containing an amount of silver halide equivalent to 6 g of silver nitrate per sq.m.

Each emulsion layer was coated with a gelatino anti-stress layer at a coverage of 1 g per sq.m.

—*Composition of the fluorescent screen material I*

The fluorescent screen used according to the invention was prepared as follows:

92.2 g of LaOBr:0.002 Tb:0.0005 Ym phosphor particles prepared according to the method described in the published German Patent Application 2,161,958 as mentioned above were dispersed in a solution of 7.8 g of ELVACITE 2044 (trade name of du Pont de Nemours, Wilmington, Del. USA for a high molecular weight poly - n - butyl methacrylate) in 21.7 g of toluene.

The dispersion obtained was filtered with a filter having passages with a mean diameter of 75 μm and was deaerated by subjecting it to a pressure of 100 mbar (100 cm of water).

The content of solids of the obtained dispersion was 82.1% by weight.

The dispersion was coated onto a subbed polyethylene terephthalate resin support of 250 μm. The subbing layer was produced from a latex on the basis of a copolymer of vinyl chloride, vinylidene chloride, n-butyl acrylate and itaconic acid (weight ratio: 63/30/5/2).

The coating of the dispersion was effected in such a way that 35 mg of phosphor were applied per sq.cm. The spectal emission characteristics of the fluorescent screen material I are the same as those represented in Fig. 1. The ytterbium is present only for reducing the "after-glow" of the phosphor.

—Composition of the fluorescent material II (Prior Art)

Europium-activated barium strontium sulphate phosphor particles prepared according to Example 7 of the United Kingdom Patent 1,322,748 filed Octber 20, 1970 by Kodak Ltd. were incorporated in an intensifying screen binder layer as described for fluorescent screen material I.

—Composition of the fluorescent screen material III (Prior Art)

Calcium wolframate phosphor screen particles of the commercial type (manufactured by Riedel-de Haën, Seelze (Hannover), W. Germany, used in $CaWO_4$ screens were incorporated in an intensifying screen binder layer as described for fluorescent screen material I.

—Exposure

The light-sensitive material was exposed to 80 kV X-ray radiation filtered through a 6 mm aluminium sheet and modulated with a test object being a line screen made of lead wherein the width of the bars of the screen gradually diminished, and their spatial frequency (number per mm) gradually increased from one side of the test object to the other. By applying such a test object in the exposure it is possible to obtain an objective value for the sharpness independently of subject contrast by determining the "square wave response function" (SWRF) (ref. Amer. J. Roentgenol. 106 (1969), pages 650—654.

A first strip of the light-sensitive material called material A was exposed between two fluorescent screen materials I arranged in contact with the opposite sides of the light-sensitive material. So were a second and a third strip called material B and C respectively, each of them between two fluorescent screen materials II and III respectively.

The exposed materials were processed in an automatic 90 seconds processing machine, the development occurring for 23 seconds at 35°C in Agfa-Gevaert's hardening developer G 138 containing hydroquinone and 1-phenyl-3-pyrazolidinone as developing agents and glutaraldehyde as a hardener.

The square wave response function of the test materials was derived from the measurements obtained by scanning the line pattern obtained in these materials with a microdensitometer.

The relative square wave response factor (value of the function) at a spatial frequency of one line pair per mm for the different combinations of light-sensitive materials and screens as defined above is listed in the following table 1.

TABLE 1

Combination of light-sensitive material and screen	Speed $S = 5-\log_{10}E$ for density : 1.00	Square wave response value at 1 line pair per mm
A, I	3.68	0.71
B, II	3.38	0.73
C, III	3.19	0.64

With the same phosphors of screens I, II and III a series of screens was made containing from 20 to 70 mg of phosphor per sq.cm and the influence of the phosphor content was studied as a function of speed. The graphs I, II and III in the accompanying Figure 2 relate to the phosphors of screen I, II and III respectively. Speed (S) is plotted versus phosphor content in mg per sq.cm. It is calculated on the basis of the formula $S=5-\log_{10}E$ wherein E is the X-ray dose at 80 kV for reaching a silver image density of 1.00 including the inherent fog density of the material. In the exposure the same silver halide recording material was used as described in the above Example.

From the graphs in Figure 2 it can be learned that the LaOBr:0.002 Tb:0.005 Yb screen-film combination yields the highest speed over the whole coverage range of 20 to 70 mg of phosphor per sq.cm.

In the accompanying Figure 3 the square wave response factors are plotted versus the speed of said screens containing from 20 to 70 mg of phosphor per sq.cm. They correspond with 0.5 line pairs/mm (curves Ia, IIa and IIIa) 1.0 line pairs/mm (curves Ib, IIb and IIIb), 2.0 line pairs/mm (curves Ic, IIc and IIIc) and 3.0 line pairs/mm (curves Id, IId and IIId). The left hand side value of each curve relates to the screen containing 20 mg of phosphor per sq.cm and the right hand side value to the screen containing 70 mg of phosphor per sq.cm.

From the curves I it can be learned that the LaOBr:0.002 Tb:0.0005 Yb screens yield a favourable combination of speed and sharpness that cannot be attained by the europium-activated barium strontium sulphate screens (curves II) and calcium wolframate screens (curves III).

When replacing in the above Example the fluorescent screen material I by a fluorescent screen material that contains instead of the LaOBr:0.002 Tb:0.0005 Yb phosphor particles a same amount of phosphor particles of the following composition:

LaOBr: 0.002 Tb
LaOBr: 0.0015 Tb
LaOBr: 0.0007 Tb

(prepared according to the United Kingdom Patent 1,247,602 as mentioned above) practically the same results were obtained.

The intensification factor for said screens under the described 80 kV exposure conditions is between 100 and 105.

When operating the fluorescent screen material I with the same silver halide materials as described in the Example, which, however, contained 7.07, 7.88, 8.73 and 9.69 g respectively of silver halide expressed as equivalent silver nitrate per sq.m the following speed and SWRF values at 1 line pair per mm were obtained.

TABLE 2

Silver halide as AgNO$_3$/sq.m	Speed $S=5-\log_{10}E$ for density : 1.00	Square wave response value at 1 line pair per mm
7.07	3.66	0.64
7.88	3.67	0.66
8.73	3.67	0.67
9.69	3.66	0.68

WHAT WE CLAIM IS:—

1. A combination of photosensitive materials suitable for radiography and comprising:

(1) a silver halide photographic material comprising a support and silver halide which is capable of producing in said material a negative silver image having a covering power (as herein defined) greater than about 50 and is present in an equivalent concentration of less than about 0.080 g of silver per sq.dm, and

(2) at least one radiographic intensifying screen material, which contains a phosphor layer comprising a phosphor or a phosphor mixture consisting wholly or mainly of a rare earth metal-activated lanthanum oxychloride lanthanum oxy-bromide, said phosphor or phosphor mixture having more than half its spectral energy emission above about 410 nm wavelength, more than half its visible light spectral emission energy between 400 and 500 nm and its maximum energy emission peak below 500 nm, and wherein said phosphor layer has a coverage

of said lanthanum oxyhalide phosphor of 100 to 800 g per sq.m and said screen material has an intensification factor of at least 20 at 40 kV and at least 25 at 80 kV.

2. The combination of claim 1, wherein said screen material contains as phosphor or phosphors one or more lanthanum oxyhalides activated with terbium or with terbium and ytterbium, said phosphors being optionally activated also with cerium and having their emission maximum in the 400—500 nm range.

3. The combination of claim 2, wherein the terbium oxyhalide content is not larger than about 0.006 mole per mole of the oxyhalide.

4. The combination of claim 2, wherein said phosphor corresponds to the following general formula:

$$La_{(1-n)}.Tb_n^{3+}OX$$

wherein:

X is chlorine or bromine

Tb^{+3} is trivalent terbium, and

n is 0.0001 to 0.006.

5. The combination of claim 4, wherein the halogen X is present in the range from 97.5 to 100% of the stoichiometric amount.

6. The combination of claim 4, wherein in the general formula n is equal to 0.002.

7. The combination of claim 2, wherein said phosphor corresponds to the following general formula:

$$La_{1-w-y}OX:Tb_wYb_y$$

wherein:

X is chlorine or bromine,

w is from 0.0005 to 0.006 mole per mole of the oxyhalide, and Y is from 0.00005 to 0.005 mole per mole of the oxyhalide.

8. The combination of claim 7, wherein w is 0.002 mole and y is 0.0005 mole.

9. The combination of claim 1 or 2, wherein the phosphor composition contains a mixture of said lanthanum oxyhalide and an yttrium oxysulphide phosphor activated with terbium.

10. The combination of materials according to any of the preceding claims, wherein the intensifying screen(s) contain(s) the fluorescent particles dispersed in a binder within the range of 80—85% by weight.

11. The combination according to any of the preceding claims, wherein the intensifying screen(s) contain(s) fluorescent particles having a grain size within the range of about 1—25 μm.

12. The combination according to any of the preceding claims, wherein said silver halide is a silver bromoiodide having an average grain size in the range of about 0.1 to 5 μm.

13. The combination according to any of the preceding claims, wherein the silver halide is coated on both sides of the support and is capable of producing a negative visible image having a covering power of about more than 50, said silver halide being present in each coating in an amount equivalent to less than about 4 g of silver per sq.m.

14. The combination described in claim 13, wherein the silver halide layers together contain an amount of silver halide equivalent to about 3 to less than about 8 g of silver per sq.m.

15. The combination of claim 13, wherein the support bears a silver halide emulsion layer on each side thereof and between said silver halide emulsion layers and/or in said emulsion layers (a) filtering dye(s) is (are) present which can be decolorized in one of the processing baths for the photosensitive silver halide material.

16. The combination of any of the preceding claims, wherein the photosensitive material comprises a support containing a filtering dye.

17. The combination according to any of the preceding claims, wherein the photosensitive material contains a filtering dye or mixture of dyes that absorb light mainly in the wavelength range of 400 to 500 nm.

18. The combination of claim 17, wherein said filtering dyes are used in a hydrophilic colloid layer.

19. The combination of claim 1, wherein the silver halide emulsion material contains silver halide on only one side of its support.

20. The combination according to any of the preceding claims, wherein said phosphor layer(s) comprise(s) particles of said phosphor or phosphor mixture dispersed in a binder, the or each such phosphor layer being carried by a support or being a self-supporting layer.

21. The combination according to any of the preceding claims, wherein the fluorescent screen(s) and the photosensitive material containing the silver halide are separate elements.

22. The combination according to any of the claims 1 to 20, wherein the fluorescent screen(s) and the support bearing the silver halide are integral parts of one element.

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1477639 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

FIG 1

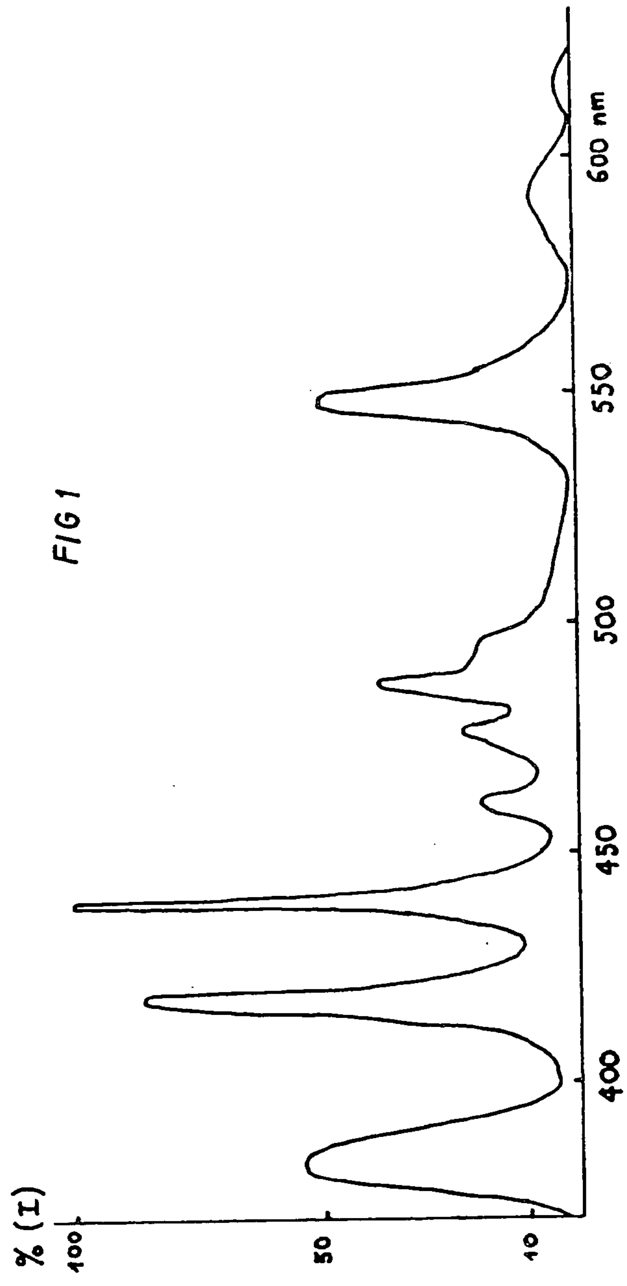


FIG 2

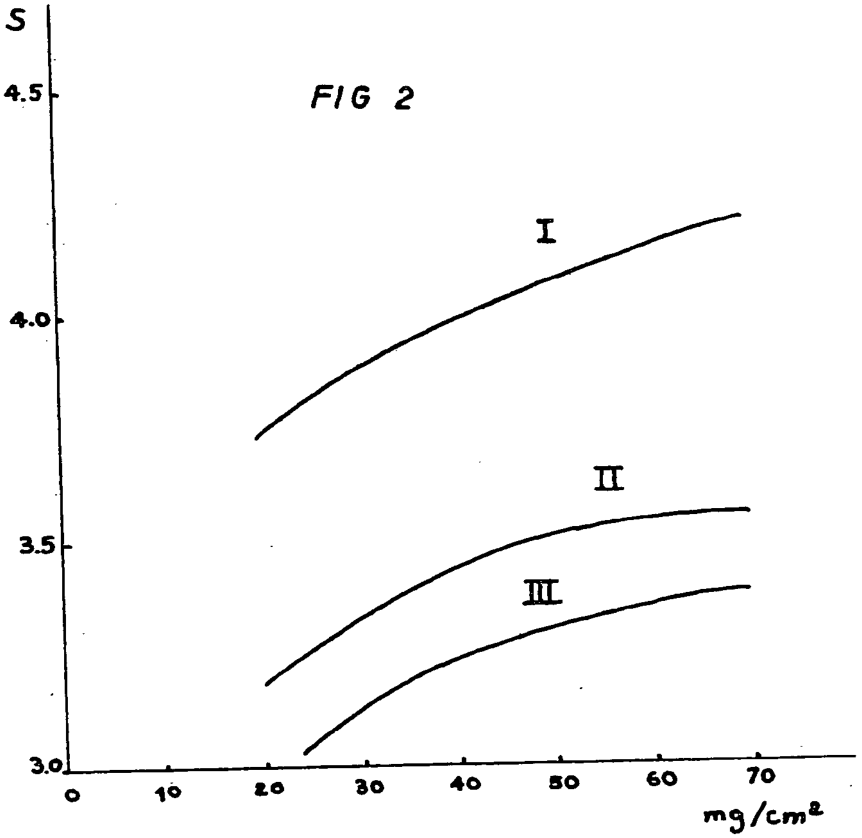
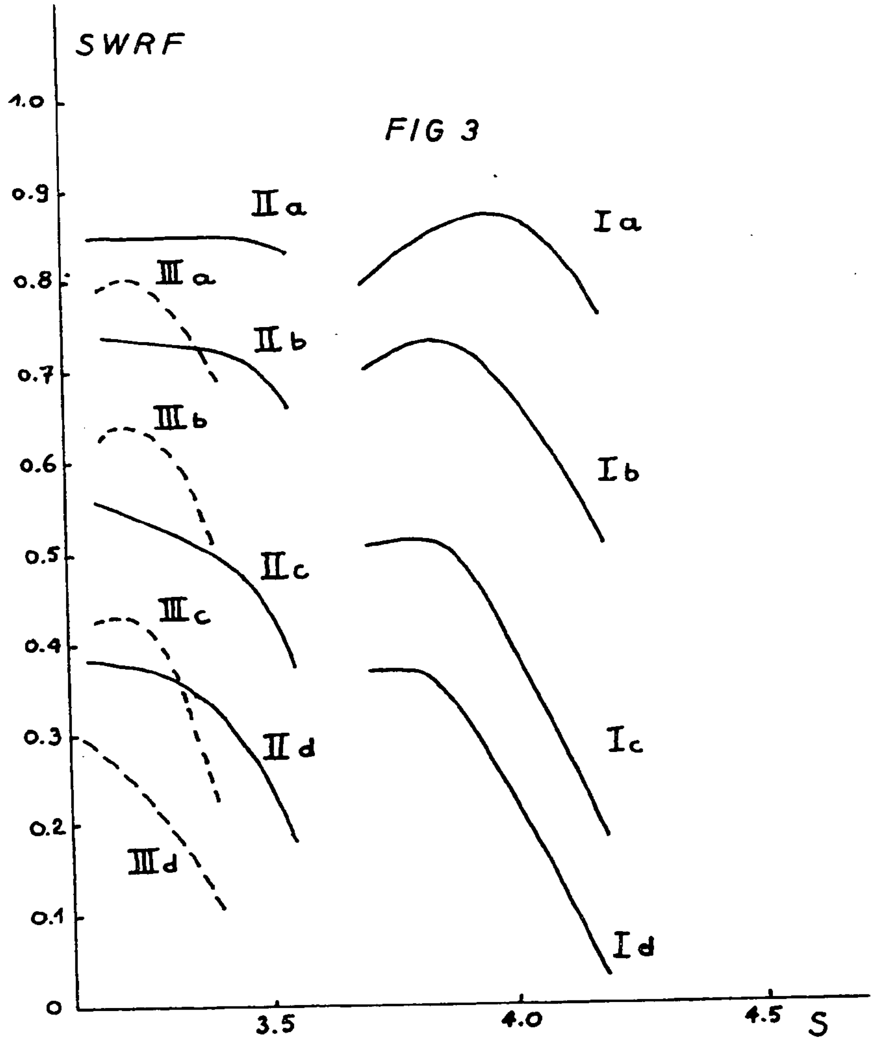


FIG 3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0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
3.5
4.0
4.5
S
IIa
IIIa
IIb
IIIb
IIc
IIIc
IId
IIId
Ia
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Ic
Id

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